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Luminescent, optical and electronic properties of La₃Ta_{0.5}Ga_{5.5}O₁₄ single crystals grown in different atmospheres

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ABSTRACT

Luminescent, optical and electronic properties of La₃Ta_{0.5}Ga_{5.5}O₁₄ single crystals grown in different atmospheres are presented. The absorption bands at 255, 290, 350 and 480 nm were detected; the intensity of bands increases with the concentration of oxygen in the growth atmosphere. It is shown that the shift of the fundamental absorption edge with the temperature obeys Urbach rule. The corresponding fitting allowed to estimate the slope coefficient σ =0.35, which implies self-trapping of excitons in La₃Ta_{0.5}Ga_{5.5}O₁₄. Calculations of the band structure, partial densities of states and reflectivity spectra were performed. The bandgap of La₃Ta_{0.5}Ga_{5.5}O₁₄ was determined as E_g =5.6 eV. The luminescence properties under UV, VUV and X-ray excitation were studied. Intrinsic emission band at 440–450 nm is attributed to the excitons self-trapped at TaO₆ molecular complexes. Extrinsic emission bands at 410, 440 and 550 nm are attributed to the emission of excitons trapped by antisite defects, F-centers and oxygen deficient oxyanionic complexes.

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1. Introduction

Lanthanum – gallium tantalate, $La_3Ta_{0.5}Ga_{5.5}O_{14}$ (langatate or LGT) is isostructural to calcium gallium germanate $Ca_3Ga_2Ge_4O_{14}$, the space group of symmetry is P321. This material has a unique combination of thermal, electrochemical and optical properties, which make it promising for application in various fields. The thermal stability of piezoelectric coefficients in LGT in contrast to other piezomaterials allowed to apply this crystal for high-temperature sensors of different physical values [1,2].

Initially grown in the 80-th, the langatate was considered as a perspective laser material, however this application has not been developed due to the insufficient optical quality of crystals. Improvement of crystals quality has been achieved recently that allows to consider LGT as a nonlinear crystal for tunable lasers with characteristics comparable to those of KTP [3]. Moreover LGT crystals are considered as suitable hosts for RE doped phosphors,

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http://dx.doi.org/10.1016/j.jlumin.2016.04.029 0022-2313/© 2016 Elsevier B.V. All rights reserved. up-conversion materials and laser crystals as well as scintillation crystals. Partial disorder of the LGT crystal structure results in the broadening of absorption lines of RE elements due to the local distortions of the crystal field. This effect results in better matching of the absorption lines with the substrate emission in LEDs. For this reason the luminescent properties of crystals doped with different rare-earth elements, have been studied [4,5,6].

The study of the origin of intrinsic defects is an important task in case of langatate. Usually the langatate crystals are grown in the inert atmosphere of Ar or N with addition of few percent of O₂, which is required to avoid evaporation of gallium oxide from the melt [7,8]. As a result the grown crystals are yellowish due to the absorption band at 480–490 nm, which is also accompanied by other absorption bands in the UV spectral region [3,9,10]. In spite of extensive studies of the optical and electric properties [11,12] the origin of those defects, which are responsible for the absorption bands, is not clear. Study of luminescent properties can provide necessary data for the identification of the origin of defect states in langatates, however this method has not been applied for such purpose so far.





The data on the luminescence of undoped LGT crystals have been presented only in a few articles [13,14,15]. A broad nonelementary luminescence band peaking at 440 nm has been observed under intraband laser excitation in [14,15]. The measurements under VUV synchrotron radiation at low temperatures allowed to separate two emission bands [13]. The band at 460 nm was related to intrinsic emission of self-trapped excitons (STE), while the band at 410 nm – to the defects of crystals structure.

The main purpose of the present study is the complex investigation of luminescent, optical and electronic properties of the undoped La₃Ta_{0.5}Ga_{5.5}O₁₄ single crystals grown in different atmospheres. It is accomplished through the combination of the experimental and theoretical methods. The paper is organized as follows: the experimental details which include the samples preparation and spectroscopic set-ups are described in Section 2. The next Section 3 makes a backbone of the paper and contains all experimental and theoretical results, divided into several subsections, followed by comparative discussion. The paper is finished with a short conclusion (Section 4).

2. Experimental details

The crystals of LGT were grown by the Czochralski method in iridium crucibles at the «Fomos-Materials» company. Single crystals of LGT were grown in different atmospheres of (i) pure argon (LGT (Ar)) and (ii) argon with admixture of 0.5% (LGT (Ar+0.5% O₂)) and 2% O₂ (LGT (Ar+2%O₂)). Plane samples with dimensions $4 \times 10 \times 1.75$ mm³ were cut from the boules. All measurements were performed from the polished surfaces of polar cut samples.

The absorption spectra of crystals were measured at 300 K using an UV–vis-NIR spectrophotometer «Cary-5000» (Agilent Technologies) and in the temperature range 78–500 K using a Jasco V-660 spectrophotometer. The samples were placed into the Janis VPF-800 cryostat. The reflection spectra were measured in the energy range 6–25 eV using synchrotron radiation at the branch-line FINEST at MAX-lab, Lund [16].

The luminescence characteristics were studied under excitation with X-rays and UV and VUV photons at T=4.2–300 K. The measurements of luminescence under X-ray irradiation were carried out using an X-ray source with a tungsten anode operating at U=40 keV. The spectra were registered using a Shamrock 500i spectrograph equipped with Newton EMCCD DU970P.

The measurements of the luminescence and excitation spectra as well as emission decay characteristics of the LGT crystals under UV and VUV excitation were performed using the laboratory setup of the Institute of Physics, University of Tartu. The measurements of luminescence excitation spectra were carried out in the energy range 2.5-8 eV using laboratory setup for VUV luminescence spectroscopy. The deuterium D 200 VUV lamp has been used as an excitation source. The samples were mounted into an optical vacuum cryostat produced by ARS, which allowed to perform measurements in the temperature range 4.2-400 K. The McPherson Model 234/302 was used as a primary monochromator and the Shamrock 303i (Andor Technology) as a secondary monochromator. Luminescence has been detected using the Hamamatsu H8259 photon counting head. The emission decay kinetics were measured with 1 µs pulses using a Xenon Perkin-Elmer FX-1152 Flashtube and an Ortec MCS-PCI Card with 100 ns resolution. The excitation wavelengths were selected with a double-quartz monochromators DMR-4. The emission was detected using an ARC SpectraPro-300i monochromator equipped with a Hamamatsu photon counting head H6240-01.

The first-principles calculations of the structural, electronic and optical properties of $La_3Ta_{0.5}Ga_{5.5}O_{14}$ were performed by means of the CASTEP module of Materials Studio package [17], using both

generalized gradient approximation (GGA) with the Perdew-Burke–Ernzerhof functional [18] and the local density approximation (LDA) with the Ceperley–Alder–Perdew–Zunger (CA-PZ) functional [19]. The plane-wave cut-off energy was set at 340 eV, the k-point grid sampling was chosen as $4 \times 4 \times 2$ with the following convergence conditions: 10^{-5} eV/atom for the energy, 0.03 eV/Å for the maximal force, 0.06 GPa for the maximal stress and 0.001 Å for the maximal displacement. The explicitly considered electronic configurations were $5s^25p^65d^16s^2$ for La, $5d^36s^2$ for Ta, $3d^{10}4s^24p^1$ for Ga and $2s^22p^4$ for O. The calculations were performed for the $1 \times 1 \times 2$ supercell.

The LGT crystallizes in the P321 space group (space group no. 150) with the following lattice constants (all in Å): a=b=8.22, c=5.124, angle $\gamma=120^{\circ}$ [20]. The optimized lattice constants (all in Å) were a=b=8.4238, c=5.2290 (GGA) and a=b=8.2052, c=5.1248 (LDA) with angle $\gamma=120^{\circ}$ in both cases. As seen from these data, the LDA-calculated results are closer to the experimental values.

The calculated electronic and optical properties of the LGT crystals will be compared below with the corresponding experimental results.

3. Results and discussion

3.1. Absorption of langatates

The optical density spectra of LGT crystals are presented in Fig. 1. Three absorption bands at 290, 360 and 480 nm can be observed in the spectra at T=300 K (Fig. 1, a), which have been also reported previously in [3,9,10]. The intensity of the absorption bands increases with the concentration of oxygen in growth atmosphere. The yellowish coloration of crystals is caused by the presence of the absorption band at 480 nm. The transparency edge in UV-region is caused by the fundamental absorption. The edge shifts to the short wavelengths with the decreasing temperature from 247 nm at T=300-238 nm at T=80 K. The shift allows to detect additional absorption band at 255 nm (Fig. 2, b). To the best of our knowledge this band has not been reported earlier.

The temperature dependence of the transparency edge can be fitted using the Urbach formula. For this purpose we use the data obtained for the LGT (Ar) crystal because the intensity of the defect-related absorption bands is the lowest in this crystal.

The absorption coefficient is an exponential function of the photon energy in the region of the fundamental absorption edge (the so-called Urbach tail). This dependence can be described by the following formula [21]:

$$\alpha(h\omega) = \alpha_0 \exp\left(-\sigma \frac{E_0 - E}{k_B T}\right),\tag{1}$$

where α_0 and E_0 are the parameters, characteristic for the given compound, k_B is the Boltzmann constant and *T* is the temperature. σ is the temperature-dependent steepness parameter, which can be represented as

$$\sigma(T) = \sigma_0 \frac{2kT}{\hbar\omega_p} \tanh\left(\frac{\hbar\omega_p}{2kT}\right),\tag{2}$$

where $\hbar \omega_p$ is the average energy of the interacting phonons and σ_0 is the limit of σ at high temperatures.

The fit of Eq. (1) to the experimental data is presented in Fig. 2. The extrapolation of the fitting lines for different temperatures intersect at a point $\alpha_0 \sim 10^4 \text{ cm}^{-1}$ and $E_0 = 5.68 \text{ eV}$. Usually the value of E_0 corresponds to the energy of exciton peak in a given compound [22,23]. This value can be used for the estimation of the bandgap of LGT taking into account that more reliable value of E_g will be slightly higher by the value of exciton binding energy. The



Fig. 1. Optical density of LGT (Ar) (1), LGT (Ar+0.5% O₂) (2) and LGT (Ar+2% O₂) (3) at T=300 K plot (a) and LGT (Ar) (1) at T=80 K (plot b).



Fig. 2. Temperature dependence of the absorption coefficient for LGT (Ar), open dots, d=1.75 mm. The lines represent the fit of Eq. (1) to the experimental data. In the inset: temperature dependence of the steepness parameter σ (squares) and it's fit by Eq. (2) (line).

 σ_0 parameter characterizes the strength of the exciton-phonon interaction and allows to predict, whether the self-trapping of excitons is expected in a given compound. The value of σ_0 below unity is a criterion for excitons self-trapping, otherwise free excitons exist. The obtained value σ_0 =0.35 is less than unity suggesting strong exciton-phonon interaction and excitons selftrapping in LGT.

3.2. Band structure of langatate

The result of the band structure calculations of LGT is presented in Fig. 3. The calculated slightly-indirect (shown by the arrow in the figure) band gaps were 3.003 eV (GGA) and 3.341 eV (LDA). The minimum of the conduction band is realized at the G point (Brillouin zone center) and the maximum of the valence band occurs along the G–F path of the Brillouin zone. Apart from this minor difference in the calculated band gap values, no considerable deviation in the profile of the electronic states was found in both cases.

The valence band (VB) is composed mainly of the 2p states of oxygen hybridized with the 5d states of Ta and La (Fig. 4). Contribution of the 3s states of Ga, which are also hybridized with the O 2p states, is concentrated at the VB bottom. The bottom of the conduction band (CB) is composed mainly of the 5d states of tantalum with some admixture of the Ga 4s states. The contribution of electronic states of lanthanum is negligible in the VB and in the lower part of the CB. The considerable contribution of the La 5d states at \sim 2 eV above the CB bottom, thus producing a well-seen second maximum in the total density of states (DOS) diagram in the CB.

Our conclusion on the origin of the Ta and O states participating in the formation of the bandgap edges, agrees with that one made on the basis of previous calculations of LGT performed in [24]. However the origin of the Ga states, which participate in formation of the VB and CB bottoms differs, e.g. the CB bottom is formed with the 4 s Ga states according to our calculations and the Ga 5 s states according to [24]. The results on the bandgap values also differ and correct estimation of this parameter is possible only using appropriate experimental data.

For additional verification of the calculation results we compared the reflectivity spectra obtained from the calculated DOS with experimental ones. The underestimation of the calculated bandgap in comparison with the experiment was overcome by introducing a scissor operator [25], which simply shifts the conduction band up-ward to bring the calculated and experimental gaps in agreement. The states of conduction band were shifted on 2.5 eV in order to get the best matching between the position of the first peak of calculated and experimental curves. The calculated bandgap in this case is about 5.6 eV that is close to the value 5.68 eV, obtained from the Urbach fitting. The comparison of experimental and calculated reflectivity is presented in Fig. 5.

The experimental reflectivity spectra were obtained for the polished samples because LGT crystals do not have perfect cleavage plane. Usually the reflectivity peaks are smoothed when the measurements are carried out from the polished surface. The smoothed reflectivity peaks can be observed at 5.8, 6.4, 8.3, and 9.4 eV in the energy range 5–11 eV. The profiles of reflectivity measured for different samples slightly differ that is probably caused by the different orientation of samples.

The calculated and experimental curves demonstrate a set of common features. The vertical lines depicted for each of the reflectivity peaks allow to trace the corresponding peaks in these curves, see Fig. 5. The first reflectivity peak is observed at 5.8 eV in LGT (Ar+0.5% O₂) as well as in the calculated reflectivity. The next peak at 6.4 eV, which is followed with a minimum at 6.9 eV is clearly seen in the reflectivity of LGT (Ar+2% O₂) and its position correspond well to that in the calculated spectrum. From three peaks observed in the calculated spectrum in the region 7.0–11.5 eV two peaks can be found in the experimental spectra at 8.3 and 9.4 eV.

The structure of the main peaks in the reflection spectra and a number of sub-peaks between 5.8–7 eV and 8–11 eV arises from the low-symmetry splitting of the 5d states of the Ta and La ions, respectively. The performed calculations allow to assign the peak observed at 5.8 eV to the electron transitions from the O 2p states from the VB top to the Ta 5d states. The peak at 6.4 eV and spectral features between 7 and 11 eV are produced by the transitions from the O 2p states. At higher energies the structure of reflectivity is determined by the electron transitions from the upper core levels. The



Fig. 3. Calculated band structure (at left) and Brillouin zone for the 1 × 1 × 2 supercell (at right) of the LGT crystal. The path along which the calculated band structure is shown, is indicated by red line.



Fig. 4. Calculated partial and total density of states diagrams for LGT. Note vertical axis break in Ga DOS diagram.



Fig. 5. Reflectivity, calculated from DOS (1) and experimental reflectivity of LGT (Ar + 0.5% O₂) (2) and LGT (Ar + 2% O₂) (3), T=300 K. The break is connected with poor flux of synchrotron radiation on the sample in the energy region 11–18 eV that did not allow to obtain reliable data.

pronounced peak at 22 eV is caused by transitions from the core 5p completely filled states of La to the unoccupied La 5d states in the CB. Less intensive peaks at 19.5 and 24.5 eV are related to the

transitions from the 3d states of Ga and 2 s states of O to the Ta 5d states and La 5d states, respectively. The intensive peak is well reproduced in the reflectivity of LGT (Ar+0.5% O₂), while less intensive peaks do not have obvious counterparts in the experimental reflectivity. However one should not expect a perfect coincidence between the experimental and calculated spectra for the high-energy region. The discrepancy between the calculated and experimental spectra at higher energies may be due to insufficient accuracy of the DFT methods for the excited states calculations [26].

3.3. Luminescent properties of langatates

3.3.1. Luminescence of langatates under X-ray excitation

A single emission band peaking at 430 nm has been observed for LGT (Ar) at T=300 K, Fig. 6(a). With cooling, its maximum shifts to 490 nm. The shift is due to the redistribution of intensities of elementary emission bands comprising the observed band. Two emission bands are clearly observed in the LGT (Ar+2% O₂) at 430 and 560 nm at T=300 K. The intensity of the latter emission band significantly increases with crystal cooling and at T=13 K this band dominates the emission spectrum. Temperature dependence of the emission bands is presented in Fig. 6(b), inset. The intensity of the short-wavelength band increases by the factor of 2 while that of the long-wavelength band increases by one order of magnitude. The similar dependences are observed for the emission in LGT (Ar) and LGT (Ar+2% O₂) that confirms the presence of two emission bands of the same origin in these crystals.

Thermostimulated luminescence has not been observed for any of the studied samples after the X-ray irradiation for up to 1 h. The presence of defect levels in the forbidden band, which may also trap charge carriers, is confirmed by the presence of absorption bands in the transparency region of LGT. The absence of thermostimulated luminescence indicates the possibility of non-radiative relaxation of the charge carries from these levels or presence of only one type (electron or hole) of traps in the LGT.

3.3.2. Site-selective luminescence spectroscopy of langatates

Luminescence spectra of LGT (Ar) are presented in Fig. 7(a). The luminescence band is peaking at 440 nm under excitation at 4.75 eV (λ_{ex} =260 nm). When excitation energy increases up to 5.15 eV (λ_{ex} =240 nm) the maximum of the band shifts to 410 nm. With further increase of excitation energy above the bandgap E_g =5.6 eV (λ_{ex} =220 and 160 nm) the position of emission band shifts to the long-wavelength region again (λ_{max} =440–450 nm)



Fig. 6. Luminescence spectra of LGT (Ar) (plot a) and LGT (Ar+2% O₂) (plot b) crystals under X-ray irradiation at T=300 K (1) and 13 K (2). In the inset: temperature dependencies of LGT (Ar+2% O₂) emission measured at 390 nm (1) and 590 nm (2).



Fig. 7. Luminescence spectra of LGT (Ar) at $\lambda_{ex}=260$ nm (1); 240 nm (2), 210 nm (3) and 160 nm (4), plot (a) and LGT (Ar + 2%O₂) at $\lambda_{ex}=260$ nm (1); 236 nm (2), 210 nm (3) and 160 nm (4), plot (b), *T*=4.2 K.

and its profile becomes broader. The luminescence excitation spectra of LGT (Ar) are presented in Fig. 8(a). To separate individual bands from the contribution of other overlapping ones, the excitation spectra were measured at the short wavelength and long wavelength slopes of the emission band, respectively. The excitation spectrum measured at the short-wavelength slope of the emission band (λ_{em} =350 nm) is characterized by a sharp peak at 240 nm. Two excitation bands peaking at 225 and 255 nm are observed when the emission is detected at the long-wavelength slope of the emission band (λ_{em} =520 nm). The position of the excitation band at 255 nm corresponds to the maximum of the absorption band, which can be observed at low temperatures. No emission has been detected under excitation at 290 and 360 nm, which corresponds to other defect-related absorption bands of LGT (Ar).

The luminescence decay curves measured at 440 nm are presented in Fig. 9. For each of the measured curves the decay is nonexponential and can be fitted at least by three or four exponential functions. When the excitation energy corresponds to the absorption band in the transparency region at 260 nm the decay curve is fitted with three exponentials with characteristic decay times 56 (2%), 490 (16%) and 1720 (82%) µs. The relative contribution of the components into the resulting decay curve is indicated in the brackets. When the excitation energy corresponds to the sharp excitation peak at 240 nm the contribution of fast components with $\tau \sim 10^{-6} - 10^{-5}$ s increases and the decay curve can be fitted with four exponential functions with characteristic decay times 29 (32%), 122 (59%), 490 (7%) and 1720 (2%) µs. With the increase of the excitation energy above the bandgap (220 nm) the slow component completely disappears from the decay curve and the curve is fitted with three decay times 21 (32%), 105 (40%) and 314 (28%) us.

The luminescence of LGT $(Ar+2\%O_2)$ under UV excitation is represented by a broad emission band with the maximum at 410– 450 nm similarly to LGT (Ar). The excitation spectra and decay kinetics are also similar to LGT (Ar). The additional features of the luminescence of LGT $(Ar+2\%O_2)$ are the following:

- In the luminescence spectra the additional emission band at \sim 550 nm is clearly observed. The relative intensity of this band increases with the increase of excitation energy. The emission band at 550 nm cannot be excited selectively;
- In the excitation spectra an additional excitation band appears, its maximum corresponds to the absorption band at 280 nm. The emission spectrum excited at 280 nm is peaking at 410 nm. The sharp peak observed in the excitation spectra at 240 nm in LGT (Ar) becomes narrower and shifts to 236 nm (probably due to the competition with another absorption bands);
- The decay curves now are characterized by the presence of an additional very long component. It contributes mostly in the decay curves measured at the low-energy excitation. The decay constants were determined under excitation at 280 nm as 84 ms (5%) and 1.53 s (95%).

3.3.3. Discussion

An influence of the growth atmosphere on the luminescent properties suggests that the defects responsible for the luminescence have rather a structural origin than are caused by inadvertent impurities. The corresponding defects can be related to the cation or anion vacancies in the LGT structure. The crystal structure of LGT is characterized by the presence of two layers, which are perpendicular to the c crystallographic axis. One layer contains the La³⁺ions in the oxygen dodecahedrons (the 3e site position), and also distorted oxygen octahedrons (the 1a site position), which are occupied by equal number of the Ga³⁺ and Ta⁵⁺ ions. Another layer contains two types of the oxygen tetrahedrons in



Fig. 8. (a) Luminescence excitation spectra of LGT (Ar) measured at λ_{ex} =350 nm (1); 450 nm (2) and 520 nm (3), *T*=4.2 K. The absorption spectrum is presented for *T*=78 K (4).(b) Luminescence excitation spectra of LGT (Ar+2% O₂) measured at λ_{ex} =350 nm (1); 450 nm (2) and 550 nm (3), *T*=4.2 K. The absorption spectrum is presented for *T*=300 K (4).



Fig. 9. Luminescence decay curves of LGT (Ar) (1) and LGT (Ar+2% O₂) (2) at λ_{ex} =220 nm (a), 240 nm (b) and 260 nm (c), λ_{em} =440 nm, *T*=4.2 K. In the inset: luminescence decay curve of LGT (Ar+2% O₂) at λ_{ex} =280 nm, λ_{em} =440 nm, *T*=4.2 K.

the 2d and 3f site positions, which are occupied by the Ga^{3+} ions only.

According to [20,27,28] in the grown LGT crystals the ratio between the Ga^{3+} and Ta^{5+} ions in octahedral coordination is not unity. The Ga^{3+} content is higher than the Ta^{5+} content and the ratio Ga/Ta is 0.54/0.46 [20], 0.523/0.477 [28] or 0.507/0.493 and

may depend on the growth atmosphere and post-growth annealing [27]. Deviation of this ratio from unity (it should be noted that these ions have different valency), violates the local electroneutrality of crystal and requires charge compensation. The charge compensation can be provided by the oxygen vacancies. It is worth noting that the growth atmosphere of LGT crystals usually contains few percent of oxygen, which is needed to prevent evaporation of gallium oxide from the crystal and allows to grow bulk crystals of larger dimensions. However it also results in the degradation of the optical quality of grown crystals because of the enhancement of absorption band (Fig. 1), which can be related to the oxygen vacancies and complexes on the basis of the vacancies (e.g. F-centers). Crystal growth in an inert atmosphere results in evaporation of gallium oxide from the crystal. We suppose that it allows to decrease the deviation of Ga³⁺ and Ta⁵⁺ content from equilibrium and grow the crystals of better optical quality.

The most part of the observed emission bands can be excited in the transparency region of the crystal and therefore are ascribed to the defect-related emission centers. Two or three emission bands, which are peaking in the blue spectral region, strongly overlap with each other. It complicates the determination of precise position of the emission bands as well as the corresponding peaks in the excitation spectra and components in the decay curves.

The emission band peaking at 440 nm is efficiently excited at 255 nm. The position of the excitation band coincides with the absorption band that allows to attribute them to the same type of defects. The emission is characterized by several decay components that may indicate non-equilibrium initial population of the excited levels of the emission center. The slow component with decay time 1.72 ms dominates in the decay curve. Such long decay time is typical for the emission of F-centers in oxides [29,30,31].

The emission band in the region of 440–450 nm is also excited by the interband excitation, however the emission decay times are considerably faster in this case. We suppose that under interband excitation the emission band at 440–450 nm has a different origin and is related to the intrinsic emission of self-trapped excitons. This conclusion is also supported by previous study of the LGT luminescence [13]. The origin of intrinsic emission centers is usually determined by the parentage of electronic states, which form the bottom of conduction band and top of valence band. In [13] it was tentatively supposed that the STE is created with the hole component at the O 2p states and electron component at the La 5d states. However, the calculations of the band structure performed in the present work demonstrate that the bottom of the conduction band is formed mainly by the 5d Ta states with some admixture of the Ga 4s states while the La 5d states form the upper part of the CB. Moreover the first peak in reflectivity is caused by the transitions from 2pO to 5dTa. The TaO_6 octahedral complexes are known as efficient emission centers, e.g. in tantalates [32,33].

The emission band at 410 nm is efficiently excited in the narrow peak below the bandgap and also can be attributed to the emission of the defects. Similar excitation characteristics are inherent also for the defect-related emission in other complex oxides, e.g. garnets and perovskites [34-36]. The corresponding emission bands are ascribed to excitons trapped near some crystal structure defect, e.g. oxygen vacancy, contaminating impurities, antisite defect or antisite defect with the oxygen vacancy nearby. The intensity of the emission band at 410 nm in LGT only slightly depends on the growth atmosphere. Therefore the defect can be scarcely attributed to the oxygen vacancy. Antisite defects exist in LGT according to [37] when Ta^{5+} substitutes Ga^{3+} in Ga(3) position. These defects usually appear due to the high crystal growth temperature and their concentration does not significantly depend on the growth atmosphere. This is consistent with the fact that the emission band at 410 nm only slightly depend on the growth atmosphere. Therefore we suppose the antisite defect to be the most probably type of defect, which traps the excitons in LGT and gives rise to the emission band at 410 nm. However we cannot completely exclude the presence of the iridium impurity in the crystal, which may be introduced into the crystal from the crucible and be responsible for the exciton trapping.

In the crystal LGT $(Ar+2\%O_2)$ the additional emission band at 550 nm and excitation band at 280 nm are revealed. The data on the luminescent properties under X-ray excitation give evidence that this band is also present in the LGT(Ar) crystal, however its intensity is considerably lower. The emission band at 550 nm cannot be excited selectively. However its relative intensity increases with the excitation energy at interband excitation. Such behavior is characteristic for the competing extrinsic and intrinsic emission bands [38,39] and confirms the defect origin of this emission band. The considerable enhancement of this band is observed with the increase of oxygen content in the growth atmosphere. From the above discussion it follows that in the LGT crystals grown in the oxygen-containing atmosphere the concentration of the oxygen vacancies increases as well. It allows to ascribe the emission band at 550 nm to the oxygen deficient oxyanionic molecular complexes, probably TaO₅ complexes.

The excitation band at 280 nm coincides with the position of the absorption band. Excitation into this band does not result in the appearance of new emission band. However this excitation band is observed in the excitation spectra of all defect-related emission bands (Fig. 8b). This indicates possibility of the energy transfer from the defect responsible for the 280 nm absorption band to the defect-related emission centers. Excitation into this band is accompanied by the appearance of a very long decay component that implies very low probability of energy transfer.

4. Conclusions

The complex investigation of luminescent, optical and electronic properties of the undoped La₃Ta_{0.5}Ga_{5.5}O₁₄ crystals grown in different atmospheres has been performed. Four absorption bands at 255, 290, 360 and 480 nm were detected in the transparency region of the langatates, their intensity increases with the concentration of oxygen in the growth atmosphere. The temperature dependence of the shift of fundamental absorption edge was fitted using the Urbach formula. The fit allowed to determine the slope coefficient σ =0.35, which indicates strong self-trapping of excitons in La₃Ta_{0.5}Ga_{5.5}O₁₄. Calculations of the band structure were

performed and verified using experimental reflectivity spectra. The bandgap value of $La_3Ta_{0.5}Ga_{5.5}O_{14}$ was determined as $E_g = 5.6$ eV.

The luminescence properties under UV, VUV and X-ray excitation were studied. The manifestation of defect centers in luminescence excitation is demonstrated. Emission bands peaking at 410, 440–450 and 550 nm were detected. The band at 440–450 nm has a complex structure and consists of two emission bands. The emission at 440 nm can be excited in the absorption band at 255 nm, it has a long decay time $\tau \sim 10^{-3}$ s and is attributed to the emission of F-centers. Under interband excitation the emission band at 440–450 nm has been observed and ascribed to the intrinsic emission of the excitons self-trapped at the TaO₆ molecular complexes. The emission band at 410 nm is efficiently excited in the narrow peak at 240 nm below the bandgap and is tentatively ascribed to the excitons trapped near antisite defects. The increase of oxygen concentation in the growth atmosphere results in a considerable enhancement of the emission band at 550 nm. The band is ascribed to the emission of oxygen deficient oxyanionic molecular complexes, probably TaO₅ complexes.

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